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Reduction of Nitriles to Amines with H_2 Catalyzed by Nonclassical Ruthenium Hydrides – Water-Promoted Selectivity for Primary Amines and Mechanistic Investigations

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Catalytic hydrogenation of nitriles to amines by nonclassical ruthenium hydride complexes derived from PNP pincer ligands is described. Aromatic as well as aliphatic nitriles are reduced to the corresponding primary amines. Hydrogen pressure influences the selectivity for the primary amines. The mechanism of nitrile reduction with nonclassical ruthenium hydride pincer complexes is investigated by DFT calculations. A catalytic cycle involving the coordination of nitrile *trans* to the pincer backbone after an initial hydride rearrangement at the ruthenium center, and the subsequent first transfer of the hydride ligand to the carbon center of the nitrile ligand is suggested as a possible reaction mechanism. Interestingly, the use of water as additive increases the selectivity for the primary amines and the rate of the reactions.

Introduction

Amines are important compounds, as they are prevalent in natural as well as synthetic chemicals. Fine chemicals and bulk chemicals industries produce assortments of amines that are widely used in pharmaceuticals, agrochemicals, polymers, and other products.[1] Selective synthesis of terminal primary amines continues to pose challenges, because these compounds are more reactive than secondary and tertiary amines.[2] Catalytic synthesis of primary amines directly from alcohols and ammonia with elimination of water is the most atom-economical method to prepare them.[3] In addition, the catalytic reductive amination of aldehydes with ammonia,[4] and the reduction of amides[5] provide alternative methods to access primary amines.

Catalytic reduction of nitriles with molecular hydrogen is a potential method for the synthesis of amines and it is a process of industrial significance. Hydrogenation of simple nitriles to amines in the presence of heterogeneous catalysts is generally carried out in the liquid phase with elevated hydrogen pressure.[2,6] For example, the key constituent of Nylon-6,6, hexamethylenediamine, is derived from adiponitrile. In organic synthesis, nitriles are commonly reduced by using stoichiometric amounts of metal hydrides such as $LiAlH_4$ or also in the presence of heterogeneous catalysts such as Pd, Ni, and Co.[7] A palladium-based heterogeneous catalytic system for the hydrogenation of nitriles in supercritical carbon dioxide was reported recently.[8]

Catalytic methods for the reduction of nitriles are well studied, and the selective catalytic methods developed in recent years highlight the further scope for synthesis of primary amines from nitriles. Beatty and Paciello used nonclassical ruthenium hydrides such as $[RuH_2(H_2)_2(PCy_3)_2]$ (**1**)[9] (PCy_3 = tricyclohexylphosphane) derived from $[Ru(cod)(methylallyl)_2]$ for the reduction of nitriles to amines.[10] Various ruthenium complexes are reported to catalyze the reduction of benzonitriles.[11] Using $[Ru(cod)(methylallyl)_2]$ as a catalyst precursor, Beller and co-workers developed in situ catalysts derived from PPh_3, DPPF (1,1′-bis(diphenylphosphanyl)ferrocene), and N-heterocyclic carbenes for the reduction of diverse nitriles to the corresponding primary amines in excellent yields and selectivity.[12] In general, most of the catalytic systems required large amounts (10 mol-%) of base such as KO*t*Bu. Recently, Sabo-Etienne reported the facile reduction of benzonitrile to benzylamine with nonclassical complex $[RuH_2(H_2)_2(PCyp_3)_2]$ (**2**)[13] ($PCyp_3$ = tricyclopentylphosphane) and suggested a mechanism for the reaction that proceeds by *ortho*-directed C–H activation within the aryl group.[14]

Tridentate pincer complexes with potential catalytic applications have been extensively studied.[15] We reported the facile one-step synthesis of **1** and its catalytic applications in Murai-type coupling of sp^2 C–H bonds with ethylene.[16] We are also interested in pincer complexes that contain nonclassical dihydrogen ligands. We reported the synthesis of the nonclassical ruthenium hydride pincer complex $[RuH_2(H_2)(PNP)]$[17] (**3**) [PNP = 2,6-bis(di-*tert*-butyl-phosphanylmethyl)pyridine; Scheme 1] and its catalytic application for efficient and selective H/D exchange between arenes

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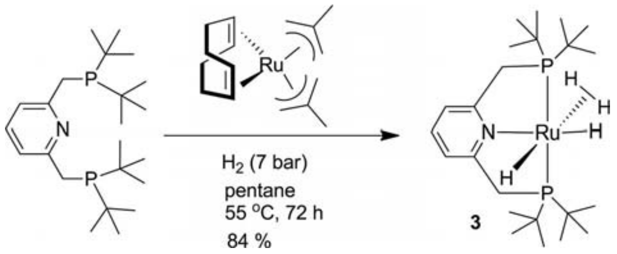
and D_2O at low temperature.[18] We report herein the reduction of nitriles with H_2 for the selective synthesis of primary amines catalyzed by **3** and the investigation of the reaction mechanism by DFT calculations. Interestingly, the addition of small amounts of water increases the rate of the reactions and the selectivity for the primary amines.



Scheme 1. Synthesis of nonclassical ruthenium hydride pincer complex **3**.

Results and Discussion

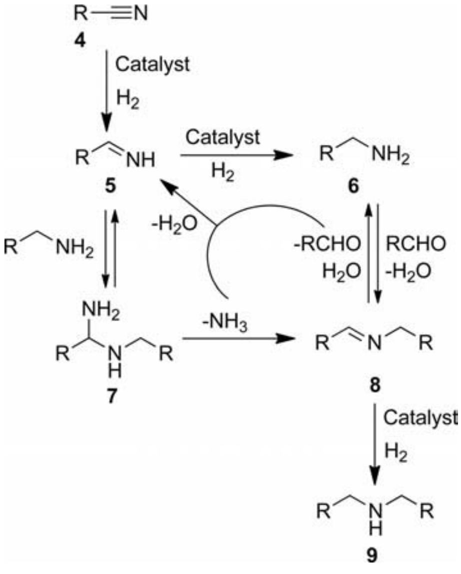
We set out to explore the catalytic activity of nonclassical ruthenium hydride pincer complex **3** for the reduction of nitriles to amines. Benzonitrile was chosen as a benchmark substrate to determine the optimal reaction conditions. Initial studies with catalyst **3** suggested that the reactions take place efficiently above 120 °C in toluene, and gratifyingly, in contrast to the many known catalytic systems for the reduction of nitriles to amines, catalyst **3** required no base. Thus, reactions were carried out with benzonitrile under neutral conditions at different H_2 pressures and reaction times with 0.25 mol-% of complex **3** as the catalyst. At low hydrogen pressures, benzylamine, dibenzylamine, and *N*-benzylidenebenzylamine were observed. Hydrogenation reactions of the nitrile functionality provided primary amines **6**. The formation of secondary amines in the reaction takes place as a result of the higher reactivity of primary amines, leading to nucleophilic attack on initially formed terminal imines **5**, and the elimination of ammonia from the unstable intermediate **7** produces the observed imines **8**, which, upon hydrogenation, yield secondary amines **9** (Scheme 2). Increasing the hydrogen pressure increases the selectivity for the primary amines (Table 1). Although a high pressure of hydrogen is not essential for the reactions to proceed, moderate selectivity for benzylamine (65%) is attained at 75 bar H_2 after 45 h (entry 5, Table 1).

Keeping 75 bar hydrogen as the pressure of choice to achieve the selectivity for the primary amines, different nitriles were subjected to hydrogenation reactions (Table 2).

Table 1. Reduction of benzonitrile by using nonclassical ruthenium hydride pincer complex **3** as catalyst.[a]

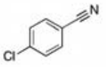
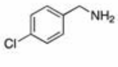
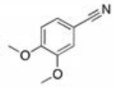
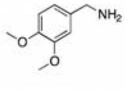
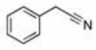
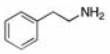
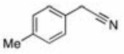
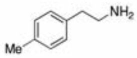
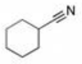
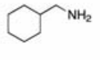
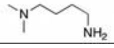
Entry	Pressure /bar	Time /h	Conv.	% Yields[b] Benzylamine	Dibenzylamine
1	25	45	99	44	23
2	40	45	98	46	25
3	60	24	98	47	19
4	60	45	99	59	20
5	75	45	>99	65	14

[a] Conditions: Complex **3** (0.01 mmol), benzonitrile (2.5 mmol), and toluene (3 mL) were charged in a steel autoclave (10 mL) under an argon atmosphere. The autoclave was pressurized with H_2 and heated at 135 °C. [b] Conversion of nitriles and product yields were analyzed by GC.



Scheme 2. Catalytic hydrogenation of nitriles with H_2. Selectivity for the primary amines is influenced by the presence of water as additive.

Table 2. Reduction of nitriles using nonclassical ruthenium hydrides pincer complex **3** as catalyst.[a]

Entry	Nitriles	Amines	*t* /h	Conv.	% Yield[b]
1			45	> 99	36[c]
2			40	> 99	88
3			45	> 99	96
4			45	99	90
5			40	99	75
6			45	> 99	82
7			24	72	57
8			45	> 99	74

[a] Conditions: Complex **3** (0.01 mmol), nitrile (2.5 mmol), and toluene (3 mL) were charged in a steel autoclave (10 mL) under an argon atmosphere. The autoclave was pressurized with H_2 (75 bar) and heated at 135 °C. Conversion of nitriles and product yields were analyzed by GC. [b] Secondary amines were present in trace amounts in all reactions, and they were not quantified. [c] Imines were also present.

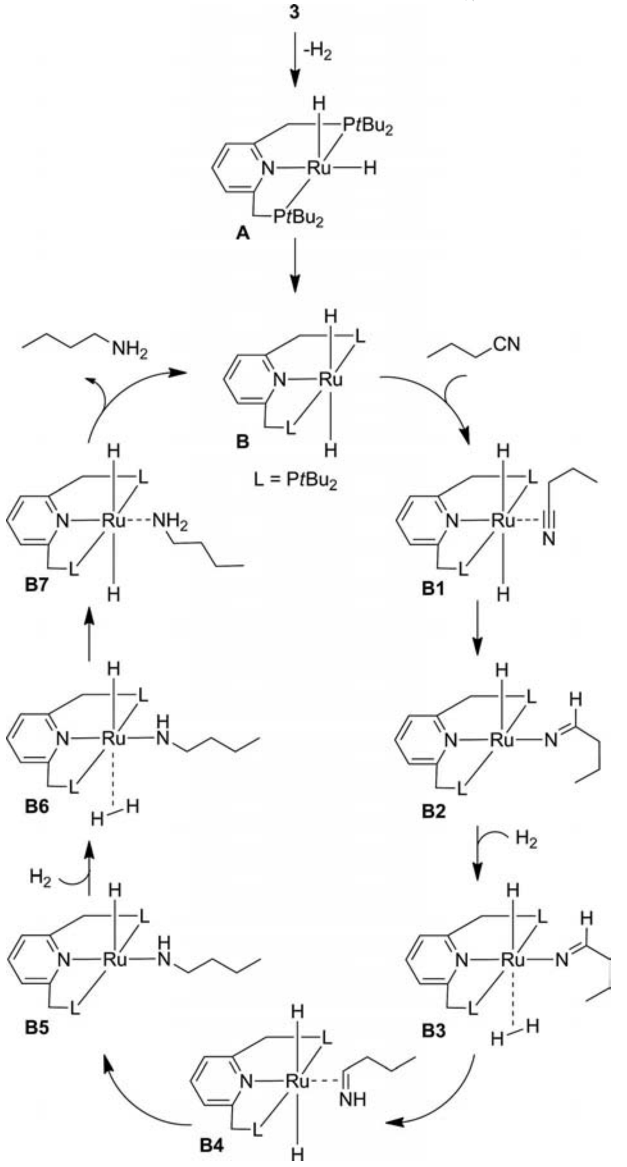
While *p*-chlorobenzonitrile exhibited poor selectivity for the primary amines, aromatic nitriles such as 3,4-dimethoxybenzonitrile displayed good selectivity for the primary amines. Similarly, other aliphatic nitriles were also reduced to the primary amines with very good selectivity (entries 3–8, Table 2).

On the basis of the above observations, the hydrogenation mechanism was investigated by means of DFT calculations for butyronitrile as the substrate in the gas phase (see Supporting Information for computational details). As shown in Scheme 3, the mechanism relies on the plausible assumption that H_2 initially dissociates from complex **3** to form complex **A**. Rearrangement of one hydrogen center leads to the formation of **B**. This rearrangement is possible in principle and therefore needs to be considered (vide infra). Both **A** and **B** are coordinatively unsaturated and can bind the nitrile. As the initial hydrogen transfer can occur either to the N or to the C atom of the nitrile moiety, four different catalytic cycles arise, which were investigated computationally. Two of these turned out to be disfavored energetically, while one cycle could not be closed, as not all transition states could be located (for details see Supporting Information). The most favored cycle is described here in detail and starts with **B**.

Starting with **B**, the coordination of the nitrile leads to the formation of **B1**. Hydride transfer from ruthenium to the carbon atom of the nitrile generates complex **B2**. Subsequent H_2 coordination to ruthenium leads to **B3**, and σ-bond metathesis of the H_2 molecule and hydride transfer to the nitrogen atom of the imide in **B3** yields complex **B4**. The second hydride is transferred to the carbon atom of imine **B4** to form **B5**, and subsequent H_2 coordination gives **B6**, followed by σ-bond metathesis of the H_2 molecule at the ruthenium center to afford complex **B7**, from which the primary amine is liberated while the catalytically active species **B** is regenerated.

All activation barriers for this cycle are well below 20 kcal/mol (Figure 1), indicating that the hydrogen-transfer steps are facile. In fact, the only activation barrier above 20 kcal/mol is the one leading from **A** to **B** (23.0 kcal/mol), which is one reason why elevated temperatures are required for the reaction to proceed. Also, the dissociation of the amine in complex **B7** to regenerate **B** requires 19.6 kcal/mol, which indicates that this step proceeds slowly. Within the framework of the energetic span model, intermediate **B7** is one of the two rate-determining states, while the second one is the transition state **TS(B4B5)**. The analysis of the energy profile with the energetic span model[19] at ambient temperature and pressure supports the experimental results quite nicely. Computationally, a TOF of 1.2 h^{-1} is predicted, while experimentally the average TOF for butyronitrile formation after 24 h is 5.9 h^{-1}, which indicates a plausible agreement between theory and experiment.[20]

Selectivity for the primary amines is often achieved in nitrile reduction reactions by the use of additives. For example, increasing the selectivity for the primary amines by the use of ammonia is well known in heterogeneous catalysis.[21] Apparently, the equilibrium between the hemiamidine **7** and



Scheme 3. Preferred calculated reaction pathway for the reduction of nitriles to primary amines with molecular H_2 in the presence of catalyst **3**.

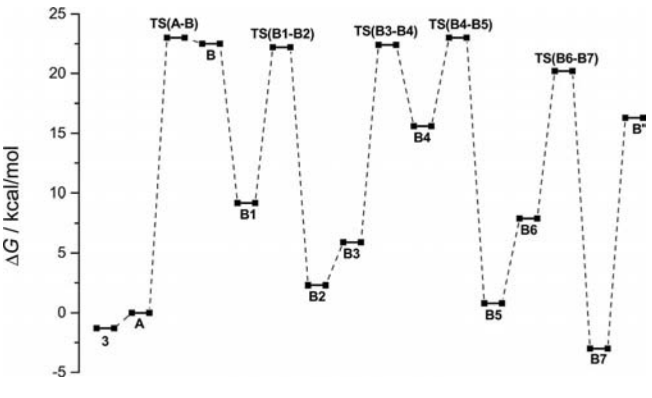
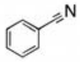
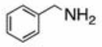
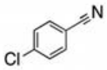
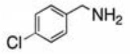
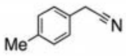
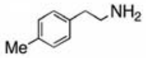
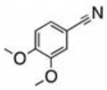
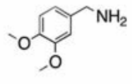
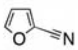
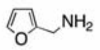
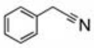
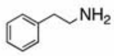
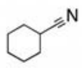
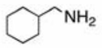
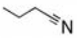
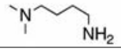


Figure 1. Energy profile for the preferred calculated reaction pathway for the reduction of butyronitrile with molecular H_2 in the presence of catalyst **3**.

terminal imine **5** shift towards **5** upon addition of excess ammonia, which leads to higher selectivity for the primary amine (Scheme 2). Very recently, nitrile reduction carried out in carbon dioxide under supercritical conditions has been reported to provide selectivity for the primary amines.[22] Complex **3** catalyzed C–H/D exchange reactions in water,[18] and reactions in water were used to increase the selectivity for the formation of primary amines in the direct coupling of alcohols and ammonia in homogeneous catalysis.[3a] Therefore, we performed the reduction of nitriles under standard conditions as described above with benzonitrile and complex **3** (0.25 mol-%) by using water as a solvent. However, benzylamine was formed only in trace amounts, while benzamide[23] was formed as a major product (43 %), in addition to the formation of benzyl alcohols. Then, we tested the possibility of using water as an additive.[24] Thus, the reactions were carried out under standard conditions with the addition of 5 equiv. of water relative to the catalyst. Although the selectivity for the benzylamine dropped to 59 % from 65 % (in the absence of water, Table 1, entry 5), a surprising increase in selectivity for *p*-chlorobenzylamine from 35 % (in the absence of water, Table 2, entry 1) to 95 % (Table 3, entry 2) was obtained. In addition, the reaction rate was almost doubled as excellent conversion of nitriles occurred in only 24 h relative to the 45 h reaction time in the absence of water (Table 1 and Table 2). In general, very good selectivity for the primary amines was obtained with various nitriles (Table 3) in the presence of water as an additive after 24 h. Furthermore, reduction of benzonitrile carried out under the standard reaction conditions with water as additive was not affected by the addition of mercury [Hg/Ru (85:1), 24 h, 64 % benzylamine], thus indicating, although not proving, that the catalytic cycles involve the homogeneous organometallic species.[25]

Table 3. Selective synthesis of primary amines: effect of water as additive in the reduction of nitriles with complex **3**.[a]

Entry	Nitriles	Amines	*t* /h	Conv.	% Yield[b]
1			24	> 99	59 (18)[c]
2			24	> 99	95
3			24	> 99	95
4			24	> 99	96
5			24	> 99	62
6			24	97	80
7			24	95	93
8			24	> 99	92
9			40	> 99	89
10			24	> 99	90

[a] Conditions: Complex **3** (0.01 mmol), nitrile (2.5 mmol), water (0.05 mmol), and toluene (3 mL) were charged in a steel autoclave (10 mL) under an argon atmosphere. The autoclave was pressurized with H_2 (75 bar) and heated at 135 °C. [b] Conversion of nitriles and yield of products were analyzed by GC. Secondary amines were present in trace amounts in all reactions, and they were not quantified. [c] Yield of dibenzylamine.

The presence of a small amount of water resulted in the concomitant hydrolysis of intermediate imines **8**, to yield primary amines **6** and the corresponding aldehydes, which could further react with ammonia to provide terminal imines **5** and water (Scheme 2), leading to the enhancement of selectivity for the primary amines and to an increase in the rates of the reactions. It should be noted that the reduction of terminal imines **5** with catalyst **3** prevails over their hydrolysis by water, which suggest that the reduction reaction may occur in an intramolecular fashion over the metal center (Scheme 3). Prolonging the reaction times further did not change the course of reaction, except that yields of primary amines decreased slightly (Table 3, entries 8,9).

Conclusions

Nonclassical ruthenium hydride pincer complex **3** displays high catalytic activity in the reduction of nitriles to amines. Although high pressure is not necessary for the reactions, better selectivity for the primary amines is achieved by using 75 bar hydrogen pressure. DFT calculations of the gas phase reaction yield four different reaction pathways, one of them being inoperative due to the absence of two transition states, which are needed to close the cycle. The cycle involving complexes in which the butyronitrile is coordinated *trans* to the pincer backbone (**B*n***) is energetically competent. The calculated TOF is 1.2 h^{-1}, while the experimental TOF is 5.9 h^{-1}, indicating nice agreement between theory and experiment. Interestingly, the use of water as additive increases the selectivity for the primary amines in addition to increasing the rate of the reactions.

Experimental Section

General Remarks: All reactions were performed under an argon atmosphere by using MBraun glove-box or Schlenk techniques. Solvents and substrates were purchased from Aldrich, Acros, and Strem Chemicals and were purified according to standard procedures. The *t*Bu-PNP ligand, 2,6-bis(di-*tert*-butyl-phosphanylmethyl)pyridine, was prepared according to the literature method.[26] Ruthenium nonclassical hydride complex **3** was prepared in a modified thick-walled glass reactor (Büchi Glas Uster

Miniclave), comparable with a Fischer-Porter bottle, according to our previously reported procedure.[17] *The use of pressurized H_2 gas can be hazardous and must only be carried out with suitable equipment and under appropriate safety precautions.*

General Procedure for Nitrile Reduction: Complex **3** (0.01 mmol), nitrile (2.5 mmol), toluene (3 mL), and water (0.05 mmol when applicable) were charged in a steel autoclave (10 mL) under an argon atmosphere. The autoclave was pressurized with H_2 (75 bar) and heated at 135 °C. Upon heating, the initial pressure reaches a value between 90 and 95 bar, and then it drops as the reaction progresses. After the predetermined reaction time, the autoclave was cooled and hydrogen was released. Mesitylene (1 mmol) was added as an internal standard to the reaction mixture, and the conversion of nitriles and yields of products were analyzed by GC (25 CW20µ-AM Macherey–Nagel column, inner diameter 0.25 mm; film thickness 0.25 µm; 50–250 °C).

Supporting Information (see footnote on the first page of this article): Computational details, alternative reaction pathways and their corresponding energy profiles, calculated energies, and Cartesian coordinates.

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